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(54) [Title of the Invention] Oxygen-Absorbing Resin Composition and Packaging Container

(57) [Abstract]

[Problems To Be Solved] To provide a resin composition comprising oxygen absorber, which has a dramatically improved oxygen absorption rate, even when blended in resin and molded, and a packaging container formed from this resin composition.

[Means For Solving the Problems] An oxygen-absorbing resin composition, characterized by comprising (A) a thermoplastic resin and (B) an iron-based deoxygenation agent comprising (B-1) iron powder and (B-2) a metal salt having a pH (25°C) of 1.0 or less when in saturated aqueous solution, the iron-based deoxygenation agent (B) being present in the amount of 1 to 100 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A) and the metal salt (B-2) being present in the amount of 0.1 to 30 parts by weight with respect to 100 parts by weight of iron powder (B-1).

[Claims]

[Claim 1] An oxygen-absorbing resin composition, characterized by comprising (A) a thermoplastic resin and (B) an iron-based deoxygenation agent comprising (B-1) iron powder and (B-2) a metal salt having a pH (25°C) of 1.0 or less when in saturated aqueous solution, the iron-based deoxygenation agent (B) being present in the amount of 1 to 100 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A), and the metal salt (B-2) being present in the amount of 0.1 to 30 parts by weight with respect to 100 parts by weight of iron powder (B-1).

[Claim 2] The oxygen-absorbing resin composition according to Claim 1, wherein the thermoplastic resin (A) is an olefin-based resin.

[Claim 3] The oxygen-absorbing resin composition according to Claim 1 or 2, wherein the metal salt is a halide of a metal of group 3B, group 4B or group 8 of the periodic table.

[Claim 4] The oxygen-absorbing resin composition according to any of Claims 1 to 3, wherein the metal salt is iron chloride.

[Claim 5] The oxygen-absorbing resin composition according to any of Claims 1 to 3 wherein the metal salt is tin chloride.

[Claim 6] A packaging container, characterized in that, in a packaging container provided with a layer of an oxygen-absorbing resin composition, said oxygen-absorbing resin composition is a resin composition comprising (A) a thermoplastic resin and (B) an iron-based deoxygenation agent comprising (B-1) iron powder and (B-2) a metal salt having a pH (25°C) of 1.0 or less when in saturated aqueous solution, the iron-based deoxygenation agent (B) being present in the amount of 1 to 100 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A), and the metal salt (B-2) being present in the amount of 0.1 to 30 parts by weight with respect to 100 parts by weight of iron powder (B-1).

[Detailed Description of the Invention]**[0001]**

[Technical Field of the Invention] The present invention relates to an oxygen-absorbing resin composition and a packaging container that uses the same; and more specifically, relates to an oxygen-absorbing resin composition with dramatically improved oxygen absorption rate within the resin and to a packaging container.

[0002]

[Prior Art] Metal cans, glass bottles, various types of plastic containers and the like have been used in the past as packaging containers, and plastic containers have been used in various applications in consideration of light weight, impact resistance and cost. However, with metal cans and glass bottles, oxygen permeability through the container walls is nonexistent, whereas with plastic containers, oxygen permeation through the container walls is at a level that cannot be ignored, and is a problem in terms of storage of the contents.

[0003] In the past, in order to trap oxygen remaining in a container or in order to trap oxygen that permeates through container walls, blending deoxygenation agents or oxygen absorbers in resin has long been known; and, in JP-57-194959-A, for example, a container lid is described which is characterized in that, in a container lid comprising a container lid shell and a sealing gasket provided on the sealing part of this shell, a solid oxygen absorber is

contained in the sealing gasket. In addition, in JP-01-278244-A, a plastic multilayer container is described which is characterized by providing a layer of a resin composition produced by blending a deoxygenation agent and a water absorber in a gas barrier resin with an oxygen permeation constant of 10^{-12} cc·cm/cm²·sec·cmHg or less at 20°C and 0% RH, and water adsorption of 0.5 wt% or greater at 20°C and 100% RH.

[0004] A material produced by coating the surface of iron powder with an oxidation accelerator or the like is known for use as oxygen absorber, and in JP-53-014185-A, an oxygen absorber is described wherein metal powder is coated with metal halide, the amount of metal halide for the coating is 0.001 to 5 parts with respect to 100 parts of metal powder, and the water content is 1 wt% or less of the entire material.

[0005] Blending an oxygen absorber produced by precoating iron powder with an oxidation accelerator is also known, and JP-57-194959-A describes the potential for using iron powder coated with a metal halide or the like as an oxygen absorber. In addition, a microporous film containing a deoxygenation agent composition is described in JP-02-072851-A, which is produced by drawing a thermoplastic resin film produced by dispersing a deoxygenation agent composition in a film; and the use of a material produced by coating the surface of iron powder with a metal halide salt as the deoxygenation agent composition is also described. In addition, in JP-06-170940-A, a method for producing an oxygen-absorbing sheet is described, which is characterized by mixing 15 to 70 parts by weight of a thermoplastic resin and a material produced by mixing electrolyte aqueous solution and 30 to 85 parts by weight of iron powder with an aggregate particle diameter of 5 to 200 μm and a primary particle diameter of 0.01 to 20 μm, carrying out sheet processing, and then drawing at 150 to 900% in at least one axial direction.

[0006]

[Problems to Be Solved by the Invention] With well-known resin compositions containing oxygen absorbers, an oxidation accelerator such as a metal halide salt adsorbs water, and oxygen that has passed through the container walls or oxygen inside the container is absorbed as a result of oxidation of the oxygen absorber such as iron powder in the presence of this water.

[0007] However, with well-known resin compositions containing oxygen absorbers, the oxygen absorption rate is excellent when the oxygen absorber is outside the resin, whereas the oxygen absorption rate is slow when blended in resin and molded; and as a result, a long time period is required for absorption of oxygen in the container, so that it cannot be said that current materials have sufficiently high oxygen absorption rates; materials also have not been adequate from the standpoint of the storage stability of contents.

[0008] Consequently, an object of the present invention is to provide a resin composition containing oxygen absorber that has a dramatically improved oxygen absorption rate even when in a molded state, and a packaging container formed from this resin composition. Another object of the present invention is to provide a sealed packaging container whereby the oxygen concentration in the container is controlled at an extremely low level, initially as well as after

a few days have passed.

[0009]

[Means for Solving the Problems] The present invention offers an oxygen-absorbing resin composition, characterized by comprising (A) a thermoplastic resin and (B) an iron-based deoxygenation agent comprising (B-1) iron powder and (B-2) a metal salt having a pH (25°C) of 1.0 or less when in saturated aqueous solution, the iron-based deoxygenation agent (B) being present in the amount of 1 to 100 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A), and the metal salt (B-2) being present in the amount of 0.1 to 30 parts by weight with respect to 100 parts by weight of iron powder (B-1).

In the oxygen-absorbing resin composition of the present invention:

1. the thermoplastic resin is an olefin-based resin; and
2. the metal salt is a halide of a metal from group 3B, 4B or 8 of the periodic table, and iron chloride and tin chloride are particularly preferred. According to the present invention, in addition, a packaging container is also provided, which is characterized in that, in a packaging container provided with a layer of an oxygen-absorbing resin composition, the oxygen-absorbing resin composition is a resin composition comprising (A) a thermoplastic resin and (B) an iron-based deoxygenation agent comprising (B-1) iron powder and (B-2) a metal salt having a pH (25°C) of 1.0 or less when in saturated aqueous solution, the iron-based deoxygenation agent (B) being present in the amount of 1 to 100 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A), and the metal salt (B-2) being present in the amount of 0.1 to 30 parts by weight with respect to 100 parts by weight of iron powder (B-1).

[0010]

[Modes of Embodiment of the Invention]

[Operation] The present invention is characterized in that, a metal salt with a pH (25°C) of 1.0 or less when in a saturated aqueous solution, preferably a halide of a metal of group 3B, group 4B or group 8 of the periodic table, and more preferably iron chloride or tin chloride, is selected from among various metal salts, and is combined with metal powder and blended in the thermoplastic resin. According to the present invention, by selecting the metal salt described above, it is possible to dramatically increase the oxygen absorption rate when blended in resin and molded.

[0011] The most commonly used water-soluble metal salt for activating iron-based deoxygenation agents is table salt (sodium chloride), but the pH of a saturated aqueous solution of sodium chloride is, of course, neutral or nearly neutral; but when this salt is admixed along with iron powder to thermoplastic resin, the oxygen absorption rate decreases by about a factor of 4 relative to the oxygen absorption rate when not blended in resin (refer to Table 1 below). In contrast, when a metal salt having a pH (25°C) of 1.0 or less as a saturated aqueous solution, and particularly a halide of a metal of group 3B, group 4B or group 8 of the periodic table, is selected as the metal salt and blended in resin, the oxygen absorption rate can increase two fold or more relative to sodium chloride, and this is an unexpected effect of the present invention.

[0012] In addition, in reference to Table 1 mentioned above, it is known that a saturated aqueous solution pH of 1.0 or less is critical for an increase the oxygen absorption rate when blended in resin.

[0013] In addition, considering the residual oxygen

concentration in a container when actually used as a container, as shown in Fig. 1, the initial oxygen absorption rate is dramatically increased when a metal salt specified by the present invention is used, in comparison to when common sodium chloride is used, and it is clear that the final residual oxygen concentration can be maintained at a dramatically reduced level.

[0014] In the present invention, the phenomenon whereby the oxygen absorption rate of the metal salt having a pH (25°C) of 1.0 or less as saturated aqueous solution is dramatically increased when blended in resin was discovered as a result of multiple experiments, and although the reason is not adequately understood, the following is presumed. Specifically, it is thought that the metal salt used in the present invention has extremely high capacity for activating iron powder covered with resin, and in addition, that hydrogen ions generated when the metal salt is in contact with water have comparatively high mobility in the resin, and play a role in the activation of the iron powder.

[0015] In the present invention, it is critical that the iron-based deoxygenation agent (B) be present in the amount of 1 to 100 parts by weight, particularly 2 to 40 parts by weight, with respect to 100 parts by weight of the thermoplastic resin (A), and that the metal salt (B-2) be present in the amount of 0.1 to 30 parts by weight, and particularly 0.5 to 10 parts by weight, with respect to 100 parts by weight of the iron powder (B-1). If the amount of iron-based deoxygenation agent (B) is below the aforementioned range, the oxygen absorption capacity will be insufficient, whereas above the aforementioned range, the moldability as a resin composition will decrease, and there will be a tendency for a decrease in the mechanical strength of the resin composition. On the other hand, if the amount of the metal salt (B-2) is below the aforementioned range, then there will be a tendency for the oxygen absorption rate to be lower than that within the range of the present invention; whereas above the aforementioned range, the water resistance and other physical properties of the resin composition as a whole will decrease, which is undesirable.

[0016] [Iron powder] A material referred to as reduced iron powder is generally used as iron powder for iron-based deoxygenation agents. Reduced iron powder is generally obtained by using a furnace and a reducer (e.g., coke) and subjecting an iron compound such as mill scale obtained in the iron ore manufacture process to finish heat treatment or finish reduction in hydrogen gas or decomposed ammonia gas. Examples of iron compounds include FeOOH, Fe(OH)₃, FeCl₃, FeSO₄ and iron oxide. Examples of iron oxides include iron ore, magnetite, limonite, siderite, iron pyrite, α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄. Other than coke, a reducing gas such as hydrogen [or] ammonia may be used as the reducer. Examples of furnaces include fluidized furnaces, rotary kilns and tunnel kilns. Finish reduction or a finishing treatment is carried out at a temperature of about 400 to 900°C. Reduction firing of the iron compound is generally carried out at a temperature of about 400 to 1300°C.

[0017] Production of the iron powder is not restricted to the above reduction method,

and production can be carried out by electrolytic deposition of iron from aqueous solution containing iron ions, spraying molten iron into a non-oxidative atmosphere, grinding pure metallic iron or steam thermal decomposition of carbonyl iron.

[0018] From the standpoint of reactivity with oxygen, it is preferable for the iron powder to have high activity, and for the amount of metallic iron to be 70% or greater. In addition, from the standpoint of preventing resin degradation and improving flavor retention, it is preferable for the content of copper to be 150 ppm or less and for the content of sulfur to be 500 ppm or less with respect to the iron.

[0019] The iron-based deoxygenation agent particles used in the present invention preferably have an apparent density of 3 g/cc or less and a specific surface area of 0.5 m²/g or greater. If the specific surface area is below 0.5 m²/g or the apparent density is above 3 g/cm³, then the oxygen absorption rate will decrease in comparison to that within the aforementioned range, and the residual oxygen amount in the container will tend to increase. This is presumably because absorption of oxygen in the resin composition containing oxygen absorber, in the end, occurs through the surface of the iron-based deoxygenation agent particles, but with particles having specific surface areas or apparent densities that are outside the aforementioned range, effective oxygen absorption from the particle surfaces does not readily occur.

[0020] In addition, the iron-based deoxygenation agent particles used in the present invention preferably have an average particle diameter of 1 to 50 μm, as measured by the laser scattering method. Iron-based deoxygenation agent particles having an average diameter that is within the aforementioned range will have superior dispersibility in the thermoplastic resin, and will also have superior oxygen absorption properties.

[0021] [Metal salt] The metal salt that is used in the present invention, as described above, has a pH (25°C) of 1.0 or less. Examples of metals are metals from group 3B, group 4B or group 8 of the periodic table, and more specifically, aluminum, tin, iron and the like may be cited. Halides, and particularly chlorides, are preferred for the metal salt, and iron chloride (FeCl₃) and tin chloride (SnCl₂) are the most preferred.

[0022] Although not always necessary, other water-soluble or water-absorbing substances may also be used in combination therewith. Specific examples include sodium chloride, calcium chloride, zinc chloride, ammonium chloride, ammonium sulfate, sodium sulfate, magnesium sulfate, disodium hydrogen phosphate, sodium diphosphate, potassium carbonate, sodium nitrate, calcium oxide, calcium sulfate, sodium hydrogen carbonate, sodium carbonate, molecular sieves, alumina, silica gel and the like.

[0023] As desired, inorganic compounds, organic compounds and macromolecular materials may be used in conjunction therewith as oxidation accelerators, and examples include glucose, fructose, sucrose, gelatin, modified casein, modified starch, tragacanth gum, polyvinyl alcohol, CMC, sodium polyacrylate, sodium alginate, ascorbic acid, sodium ascorbate, polyethylene oxide, polyacrylamide, polyoxyethylene, EDTA, EDTA-2Na, EDTA-4Na and the like. These oxidation accelerators may be blended in the thermoplastic resin in the form of the deoxygenation agent particles, or may be blended in the resin separate from the deoxygenation agent particles. Of

course, in the present invention, it goes without saying that multiple oxidation accelerators or catalysts may be used in combination.

[0024] [Composite deoxygenation agent] In the present invention, iron powder and metal salt are blended in the thermoplastic resin in the weight ratios described above. The iron powder and metal salt can be blended separately in the thermoplastic resin, but in general, it is preferable to blend the iron powder and metal salt in advance, and to then blend this blended composition with the thermoplastic resin.

[0025] In this deoxygenation agent, it is preferable for the iron powder (B-1) and metal salt (B-2) to be blended at a weight ratio of 100:0.1 to 100:30, and particularly 100:0.5 to 100:10. If the ratio of the amount of metal salt falls below this range, the oxygen absorption rate will tend to decrease relative to that within the aforementioned range, and if the ratio of the amount of metal salt is above this range, then the water resistance or mechanical characteristics will tend to decrease in comparison to that within the aforementioned range.

[0026] In the present invention, blending of the iron powder and metal salt can be carried out by dry blending using a V-type blender, conical blender, super mixer, Henschel mixer or the like. In addition, the metal salt can be coated and fixed onto the surfaces of the iron powder, and this fixed coating is carried out by dry milling the iron powder with metal salt powder. The end point of dry milling can be determined by confirming with an electron microscope that there are no free solid particles of metal salt. A vibration mill, ball mill, tube mill, super mixer or the like can be used in dry milling. In addition, wet coating of metal salt onto the iron powder surfaces can be carried out, and this wet coating is carried out by spraying an aqueous solution or organic solvent solution (e.g., ethanol, acetone or ether) of the metal salt onto the iron powder, or by impregnating the iron particles and then removing the solvent. With the deoxygenation agent particles obtained after dry milling or wet mixing, the free metal salt micropowder can be separated and removed by sieving, air-sizing or an other operation, although this is generally not necessary.

[0027] [Oxygen-absorbing resin composition] According to the present invention, an iron-based deoxygenation agent (b) [sic] is blended in the amount of 1 to 100 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A), and metal salt is blended in the amount of 0.1 to 30 parts by weight with respect to 100 parts by weight of the metal powder.

[0028] Examples of thermoplastic resins include any of the following resins: polyolefins such as low-density polyethylene, linear low-density polyethylene (LLDPE), high-density polyethylene, polypropylene, poly-1-butene,

poly-4-methyl-1-pentene, ethylene, propylene, 1-butene, 4-methyl-1-pentene or other α -olefin random or block copolymers; ethylene-vinyl acetate copolymer, ethylene-vinyl alcohol copolymers, ethylene-vinyl chloride copolymers and other ethylene-vinyl compound copolymers; polystyrene, acrylonitrile-styrene copolymers, ABS, α -methylstyrene-styrene copolymer and other styrene-based resins; polyvinyl chloride, polyvinylidene chloride, vinyl chloride-vinylidene chloride copolymers, polymethyl acrylate, polymethyl methacrylate and other polyvinyl compounds; nylon 6, nylon 6,6, nylon 6,10, nylon 11, nylon 12 and other polyamides; polyethylene terephthalate, polybutylene terephthalate and other thermoplastic polyesters; polycarbonate; and polyphenylene oxide and mixtures thereof.

[0029] From the standpoint of rapid elimination of oxygen, it is preferable for the thermoplastic resin in which the deoxygenation agent is blended to be permeable to oxygen, and olefin-based resins are particularly suitable in this regard. On the other hand, although olefin-based resins have low water retention capacity and cause swelling of the resin layer, by using the aforementioned deoxygenation agent, the required water supply for oxygen absorption can occur smoothly. In addition, in order for the thermoplastic resin containing a deoxygenation agent to retain barrier properties over a long period of time, materials having low oxygen permeability are preferred, and ethylene-vinyl alcohol copolymers or polyethylene terephthalate resin are suitable in this regard.

[0030] In the present invention, using a blend of numerous thermoplastic resins or elastomers that are substantially incompatible as the resin matrix in which deoxygenation agent is blended is preferred from the standpoint of improving external appearance.

[0031] Examples of thermoplastic elastomers that may be cited include ethylene-propylene rubber (EPR), ethylene-propylene-diene rubber (EPDM), thermoplastic elastomers such as styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymer, hydrogenated styrene-butadiene-styrene block copolymer, hydrogenated styrene-isoprene-styrene block copolymer, hydrogenated butadiene-isoprene block copolymer, nitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), polybutadiene (BR), polyisoprene (IIB), butyl rubber, natural rubber, thermoplastic polyurethane, silicone rubber, acrylic rubber, and the like. Among these, hydrocarbon-based elastomers, and particularly EPR or EPDM, are desirable.

[0032] In the present invention, combinations of mutually incompatible thermoplastic resins or elastomers include, but are not restricted to, propylene-based polymer/ethylene-based polymer, polyamide/olefin-based resin, polyamide/styrene-based resin, polyamide/ABS resin, polyethylene terephthalate/polybutylene terephthalate, polycarbonate/polystyrene-based resin, polyester resin/olefin-based resin, polycarbonate/polyester resin, and the like.

[0033] Dispersion and hot-molding of the deoxygenation agent are easy, and particularly desirable resin combinations are combinations of crystalline polypropylene-based polymers and ethylene-based polymers. In addition to homopolypropylene, random or block copolymers containing 1 to 20 wt%, particularly 2 to 15 wt%, of ethylene are used as the crystalline propylene-based polymer. These polypropylenes may be

materials with isotactic structures or materials with syndiotactic structures.

[0034] Examples of ethylene-based polymers include high-density polyethylene (HDPE), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), copolymers of ethylene and at least one other olefin such as propylene, butene-1, pentene-1, hexane-1,4-methylpentene-1, octene-1 or decene-1, ethylene-vinyl acetate copolymer, ethylene-acrylate copolymer and ionomers.

[0035] Although the ratio of one resin and the other resin in the composite resin matrix can be varied over a broad range, the weigh ratio is preferably in the range of 100:1 to 1:1, particularly 50:1 to 3:2.

[0036] A compatibilizing agent may be blended in this composite resin matrix in order to adjust the degree of interdispersion of resin or elastomer. The compatibilizing agent increases interactions between different types of polymers, and is a block copolymer or graft copolymer having the same components as polymer A and B that are blended; a block copolymer or graft copolymer having a third component that mixes at the molecular level with either polymer A or B that are blended; or a graft copolymer of two types of polymer that are compatible with only one of the polymer A or B that are blended.

[0037] In addition, there are two types of compatibilizing agents based on function: non-reactive compatibilizing agents and reactive compatibilizing agents, where examples of the former include styrene-ethylene-butadiene block copolymer, polyethylene-polymethyl methacrylate block copolymer and polyethylene-polystyrene block copolymer, whereas examples of the latter include maleic anhydride-modified olefin-based resin, particularly maleic anhydride graft polypropylene or polyethylene, styrene-maleic anhydride copolymer, ethylene-glycidyl methacrylate copolymer, ethylene-acrylic acid ester-maleic anhydride copolymer, styrene-glycidyl methacrylate copolymer, and the like.

[0038] These compatibilizing agents can be present in amounts of 1 to 20 wt% in the resin matrix, and particularly

2 to 10 wt%.

[0039] Mixing of the deoxygenation agent and resin matrix may be carried out by so-called dry blending or melt blending, or alternatively, a resin composition (master batch) containing a high concentration of deoxygenation agent can be produced, and this master batch can be blended with the resin matrix in order to facilitate dispersion of the deoxygenation agent.

[0040] [Packaging container] The oxygen-absorbing packaging container of the present invention can have any layered structure, provided that the thermoplastic resin layer containing the deoxygenation agent is provided in the container walls. In general, from the standpoint of the external appearance of the container or sanitation with respect to the contents, thermoplastic resin layer not containing deoxygenation agent is preferably laminated to both sides of the resin composition containing deoxygenation agent.

[0041] An example of a multilayer structure for the packaging container of the present invention is presented in Fig. 2, wherein the container wall 1 comprises a moisture-resistant thermoplastic resin outer layer 2, an adhesive resin layer 3a, a gas barrier resin first intermediate layer 4, an adhesive resin layer 3b, a second intermediate layer 5 comprising the resin composition containing deoxygenation agent and a moisture-resistant thermoplastic resin inner layer 6. The second intermediate layer 5 is a thermoplastic resin layer in which the deoxygenation agent is blended, and this thermoplastic resin may comprise resin with a simple composition, or multiple thermoplastic resins or elastomers that are substantially incompatible. It should be noted that the second intermediate layer is situated inside of the gas barrier resin layer 4.

[0042] Another example of a multilayer structure for the packaging container of the present invention is presented in Fig. 3, wherein the container wall 1 comprises a moisture-resistant thermoplastic resin outer layer 2, an adhesive resin layer 3a, a first intermediate layer 4 comprising a gas barrier resin, an adhesive resin layer 3b, a second intermediate layer 5 comprising the resin composition containing the deoxygenation agent, a third intermediate layer 7 comprising resin composition containing an adsorbent deodorant and a moisture-resistant thermoplastic resin inner layer 6. The deoxygenation agent and adsorbent deodorant are each individually blended in the second intermediate layer 5 and third intermediate layer 7, and it is to be understood that the sequence, from the exterior, is: gas barrier resin layer 4, deoxygenation agent layer 5, and adsorbent deodorant layer 7.

[0043] A moisture-resistant resin (low hygroscopic resin), specifically a thermoplastic resin with a water absorption, measured according to ASTM D570, of 0.5% or less, and particularly 0.1% or less, is suitable as the thermoplastic resin layer that is provided on both sides of the resin layer containing the deoxygenation agent. Typical examples include low-, medium- or high-density polyethylene, isotactic polypropylene, ethylene-propylene copolymer, polybutene-1, 4-methyl-1-pentene, ethylene-butene-1 copolymer, propylene-butene-1 copolymer, ethylene-propylene-butene-1 copolymer, ethylene-vinyl acetate copolymer, ion crosslinked olefin copolymer (ionomer), blends thereof and other olefin-based resins, and, in addition, polystyrene, styrene-butadiene copolymer, styrene-isoprene copolymer, ABS resin and other

styrene-based resins, polyethylene phthalate, polytetramethylene terephthalate and other thermoplastic polyesters or polycarbonate may also be cited. Among these, olefin-based resins are preferred from the standpoint of sanitation, and propylene-based resins are preferred from the standpoint of heat resistance.

[0044] A thermoformable thermoplastic resin that has a low oxygen permeability constant is used as the gas barrier resin that is used as desired in the packaging container of the present invention. The most preferred examples of gas barrier resins that can be cited are ethylene-vinyl alcohol copolymers; for example, a copolymer saponification product is used that is obtained by saponifying ethylene-vinyl acetate copolymer with an ethylene content of 20 to 60 mol%, particularly 25 to 50 mol%, so that the saponification level is 96 mol% or greater, and particularly 99 mol% or greater. This ethylene-vinyl alcohol copolymer saponification product should have a molecular weight sufficient for allowing film formation, and in general, preferably has a viscosity of 0.01 dL/g or greater, particularly 0.05 dL/g or greater, when measured at 30°C in a phenol:water mixed solvent with a weight ratio of 85:15.

[0045] In addition, as examples of other gas barrier resins that have the characteristics described above, polyamides wherein the number of amide groups per 100 carbon atoms is in the range of 5 to 50, particularly 6 to 20, can be used, e.g., nylon 6, nylon 6,6, nylon 6/6 [sic], hexamer, metaxyllylene adipamide, nylon 6,10, nylon 11, nylon 12 and nylon 13. These polyamides also are to have a molecular weight sufficient for film formation, and it is preferable for the relative viscosity (η_{rel}) measured at a temperature of 30°C in sulfuric acid at a concentration of 1.0 g/dL to be 1.1 or greater, particularly 1.5 or greater. Note that these gas barrier resins, as shown in Fig. 2, are provided adjacent to the resin layer containing the deoxygenation agent.

[0046] As with the ethylene-vinyl alcohol copolymer, there are cases where insufficient adhesion is obtained when laminating gas barrier resins and moisture-resistant thermoplastic resins, but in such cases an adhesive resin layer is interposed between the two.

[0047] Examples of this type of adhesive resin include thermoplastic resins comprising carboxylic acid, carboxylic anhydride, carboxylic acid salt, carboxylic acid amide or carboxylate ester with a concentration of 1 to 700 meq/100 g resin, particularly 10 to 500 meq/100 g resin, of

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carbonyl O groups in their primary chains or side chains. Suitable examples of adhesive resins are ethylene-acrylic acid

copolymer, ion crosslinked olefin copolymers, maleic anhydride grafted polyethylene, maleic anhydride grafted polypropylene, acrylic acid grafted polyolefin, ethylene-vinyl acetate copolymer, copolymer polyester and copolymer polyamide, alone or in combinations of two or more types. These resins are useful in co-extrusion or in lamination by means of sandwich lamination or the like. In addition, isocyanate-based, epoxy-based or other thermosetting adhesive resins may also be used in the adhesive layer between the moisture-resistant resin film and gas barrier resin film formed in advance. In addition, metal foil such as steel foil or aluminum foil may be used instead of gas barrier resin.

[0048] It is generally preferable for the resin layer containing the deoxygenation agent to have a thickness of 5 to 200 μm , and particularly 10 to 150 μm , although this will differ depending on the allowed oxygen level in the container and the container shape.

[0049] On the other hand, the moisture-resistant resin layer provided on both sides of the resin layer containing the deoxygenation agent generally has a thickness of 10 to 500 μm , and particularly 20 to 200 μm , and is preferably 0.05 to 100x, and particularly 0.5 to 10x, relative to the thickness of the intermediate layer. The thicknesses of the inner layer and outer layer may be equivalent, or a structure may be produced in which either the inner layer or outer layer has a thickness that is greater than the other. In addition, the thickness of the gas barrier resin layer generally preferably has a thickness of 5 to 100 μm , particularly 10 to 50 μm .

[0050] The packaging container of the present invention can be produced by a method that is well known *per se*. For example, the container can be produced by multilayer co-extrusion, and after melt-kneading the resins or resin compositions using an extruder for each of the resin layers, extrusion is performed in the desired shape through multilayer multiple dies such as T-dies or circular dies. In addition, after melt-kneading the resin or resin composition with injectors for each of the resin layers, a multilayer container or a preform for the container are produced by co-injection or sequential injection into an injection mold. In addition, a lamination format such as dry lamination, sandwich lamination or extrusion coating may also be used.

[0051] The molding can have the form of a film, a sheet, a parison or pipe for bottle or tube formation or a preform for bottle or tube molding. Formation of a bottle from a parison, pipe or preform is readily carried out by pinching off the extruded material with a pair of split molds, and then blowing the liquid therein. In addition, after cooling the pipe or preform, it can be heated to the drawing temperature and by carrying out blow-drawing in the circumferential direction as a result of liquid pressure along with drawing in the axial direction, a blow-drawn bottle or the like can be obtained.

[0052] In addition, by subjecting the film or sheet to means such as vacuum molding, pressure molding, inflation molding or plug assist molding, a packaging container that is cup-shaped, tray-shaped or the like can be obtained. In addition, with multilayer films, the film may be superimposed in a pouch-form or folded and the periphery may be heat-sealed to produce a pouch-form container.

[0053] [Package] The packaging container of the present invention is useful as a sealed packaging container in which the contents are heated by hot sterile water, hot-filled, retort sterilized or the like; and, in addition, when a gas barrier resin is used, is useful as a cooking packaging container

wherein the sealed contents are opened and heated with a microwave or the like. There are no particular restrictions on the filling contents, but from the standpoint of oxygen absorption, contents having a water content of 5% or greater are particularly appropriate.

[0054] When a gas barrier resin is used instead of metal foil as the barrier material, under normal conditions, it is the gas barrier resin layer that serves to prevent oxygen permeation as an oxygen shield, but under conditions in which water and heat act simultaneously as with heat sterilization, the deoxygenation agent present in the intermediate resin layer effectively serves as an oxygen shield, and thus allocation of functionality effectively occurs depending on the conditions in which the container is placed. Specifically, under conditions in which water and heat act simultaneously, permeation of water through the moisture-resistant resin layer is marked, and the gas barrier resin undergoes a decrease in its intrinsic oxygen barrier performance resulting from this moisture and the increase in temperature, but the deoxygenation agent is activated by the absorbed water and applied heat, and thus the oxygen is effectively trapped by the deoxygenation agent and, as a result, permeation of oxygen is inhibited during heat sterilization.

[0055]

[Working Examples] The present invention is further described below by means of examples.

[0056] Working Example 1

Iron powder and additives were mixed in a V-type mixer, and a deoxygenation agent was produced with an additive amount of 3.5 wt%. Next, a pelletizer comprising a twin-screw extruder, strand die, chiller and cutter was used, and a pellet was produced which was blended at 25 wt% with polypropylene having a MI of 1. The pellet was then formed into a thin sheet using a hot press to produce samples for oxygen absorption measurement. The oxygen absorption amounts of the deoxygenation agent and deoxygenation agent blended resin were determined by introducing the sample and 1 mL of water into an oxygen-impermeable aluminum foil laminate cup without allowing the two to intermix, heat sealing using an oxygen impermeable aluminum foil laminate lid in open air, storing for 1 day at 50°C, measuring the oxygen concentration in the container with a gas chromatograph, and then finding the change in oxygen concentration (initial volume 73 mL (STP), initial oxygen concentration 20.9%). The pH of the additives that were used were measured at 25°C with a pH meter (HM-30S glass electrode GST-5311C, manufactured by Toa Electronics) using a saturated solution of distilled water. The results are presented in Table 1. The absorption amounts were expressed as values calculated relative to 1 g of deoxygenation agent.

[0057] No dramatic difference in oxygen absorption was seen between the deoxygenation agents wherein the additive was the product of the present invention (FeCl_3 , SnCl_2) and those wherein the additive was a comparative control product, but there was a dramatic difference when blended with the resin, and the product of the present invention wherein the deoxygenation agent was an additive that produced a pH of 1 or less in saturated solution was superior.

[0058]

[Table 1]

Oxygen absorption for deoxygenation agents and resin product containing a deoxygenation agent

Additive		Oxygen consumption/ml (STP)/grams deoxygenation agent		
		pH	Deoxygenation agent	Resin blend
Product of the present invention	SnCl ₂	0	255	149
	FeCl ₃	0	255	185
Comparative control product	NaCl	6	253	73
	MgCl ₂	6	260	47
	CoCl ₂	2	259	109

[0059] Working Example 2

A deoxygenation agent produced by the same method as in Working Example 1 was blended at 25 wt% in linear low-density polyethylene (LLDPE) with a MI of 2, and pellets were produced. Next, a film was produced that comprised a resin layer containing the deoxygenation agent, a urethane-based adhesive layer and a LLDPE layer. The film thicknesses were 50 μ m for the resin layer containing

the deoxygenation agent, 5 μ m for the adhesive layer and 15 μ m of the polyethylene layer. The material was cut into squares with sides of 30 mm, and the oxygen absorption amount was measured at a storage temperature of 22°C using the same method as in Working Example 1. The results are presented in Table 2.

[0060]**[Table 2]**

Oxygen consumption of film

Additive		Oxygen consumption/ml (STP)/cm ²		
		1 day	1 week	2 weeks
Product of the present invention	FeCl ₃	0.09	0.26	0.30
	SnCl ₂	0.06	0.19	0.23
Comparative control product	NaCl	0.01	0.03	0.04
	MgCl ₂	0.04	0.14	0.16

[0061] Working Example 3

A deoxygenation agent was produced by the same method as in Working Example 1, and pellets having the same composition as in Working Example 2 were produced. These pellets were used, and a film comprising an LLDPE layer and resin layer containing the deoxygenation agent was inflation molded. In addition, lamination of PET and aluminum film was carried out using a urethane-based adhesive. The film structure of the film was PET 12 μ m, aluminum foil 7 μ m, adhesive layer, deoxygenation agent blended resin layer 50 μ m, LLDPE layer 15 μ m. This laminate film was used as the lid member (surface area 32 cm²) for an oxygen-impermeable cup, water was added to the container, which was stored at 22°C, whereupon the change in oxygen concentration in the container was measured (initial head space 20 mL (STP), initial oxygen concentration 20.9%). The results are presented in Fig. 1.

[0062]

[Effect of the invention] According to the present invention, by selecting from among water-soluble salts a metal salt with a pH (25°C) of 1.0 or less when in saturated aqueous solution, combining this with iron powder, and blending with thermoplastic resin, a dramatically improved oxygen

absorption rate is achieved even when blended in resin and molded; and a sealed packaging container can be provided whereby the oxygen concentration in the container can be suppressed to extremely low levels, initially as well as after a few days have passed.

[Brief Description of the Drawings]

[Fig. 1] Graph showing the relationship between oxygen concentration in the container and time.

[Fig. 2] Sectional view showing an example of the multilayer structure of the container of the present invention.

[Fig. 3] Sectional view showing another example of a multilayer structure of the container of the present invention.

[Description of the Reference Numerals]

- 1 Container wall
- 2 Moisture-resistant thermoplastic resin outer layer
- 3a, 3b Adhesive resin layers
- 4 First intermediate layer comprising gas barrier resin
- 5 Second intermediate layer comprising resin composition with blended deoxygenation agent
- 6 Moisture-resistant thermoplastic resin inner layer
- 7 Third intermediate layer comprising resin composition with blended adsorbent deodorant

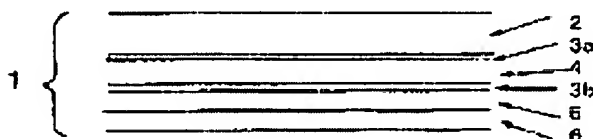
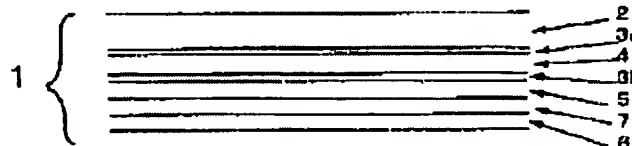
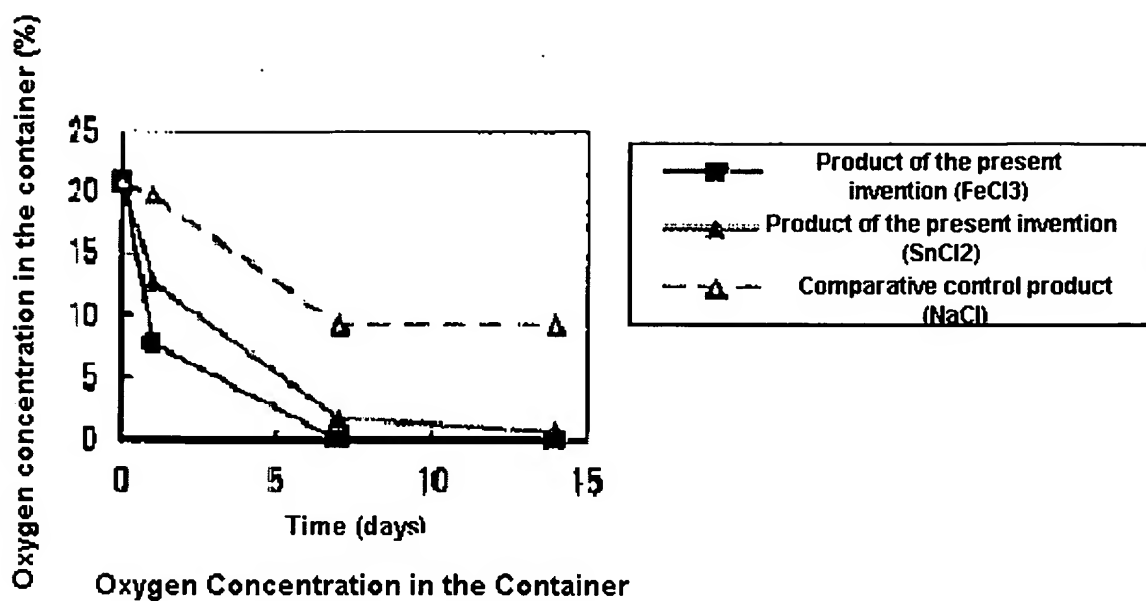
FIG. 2**FIG. 3**

FIG. 1



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